

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-01-

Public reporting burden for this collection of information is estimated to average 1 hour per response, including gathering and maintaining the data needed, and completing and reviewing the collection of information. Send collection of information, including suggestions for reducing this burden, to Washington Headquarters Service, Paperwork Project, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Project, Suite 1204, Arlington, VA 22202-4302.

rces,
f this
erson

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE	3. REPORT TYPE AND DATES COVERED Final - 1 April 1998 - 31 March 2001	
4. TITLE AND SUBTITLE AASERT 98: Investigations of New Classes of Molecular Materials			5. FUNDING NUMBERS F49620-98-1-0406	
6. AUTHOR(S) Dr. A. Welford Castleman, Jr. Department of Chemistry				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Pennsylvania State University 152 Davey Laboratory University Park, PA 16802			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 801 North Randolph Street, Room 732 Arlington, VA 22203-1977			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR) NOTICE OF TRANSMITTAL DTIC. THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLIC RELEASE LAW AFR 190-12. DISTRIBUTION IS UNLIMITED.				
12a. DISTRIBUTION AVAILABILITY STATEMENT Distribution Unlimited: Approved for public release			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) As one phase of our recent program, we undertook studies to determine accurate values of the ionization potentials of Met-Cars. Attention was directed to determining the shapes of the threshold functions for the titanium and zirconium systems. The findings are of value in furthering knowledge of the electronic properties, but also in order to understand their structures. Particular attention continued to be focused on both the pure-metal and mixed-metal Met-Cars of the stoichiometry $Ti_{1-x}Zr_xCr_2$ ($x = 0-4, 8$) since these are species where there have been particular discrepancies with the literature values. As discussed below, knowledge of their IP's is also important to unravel the unique observed delayed ionization of these species. In addition, comparison between theoretically predicted and experimentally measured IP's provides a good test for both types of investigation, which hence bridges the gap between theoretically constructed pictures of Met-Cars and experimental observations.				
14. SUBJECT TERMS			15. NUMBER OF PAGES 25	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT U		18. SECURITY CLASSIFICATION OF THIS PAGE U	19. SECURITY CLASSIFICATION OF ABSTRACT U	20. LIMITATION OF ABSTRACT

20010625 156

AASERT98: Investigations of New Classes of Molecular Materials

I. Introduction

Materials of finite size often display properties that differ from those of similar bulk compositions and currently there is extensive interest in the prospect of developing new materials that can be tailored to display unique characteristics. Indeed, through the concept of cluster assembly, there is the promise of designing and producing ones that may exhibit unique optical, electronic, or structural properties on the one hand, or perhaps useful catalytic or reactive characteristics on the other. The overall goal of our ongoing AFOSR sponsored programs is to provide underpinning basic research that will serve as a foundation for accomplishing the above mentioned goals, with attention to producing nanoscale materials with potential value for a variety of Air Force applications. The work comprises studies devoted to a determination of the dynamical properties, structure, and stability of selected cluster systems that show particular promise in reaching these goals. Attention is focused on studying Met-Cars, a class of cage-like transition metal-carbon clusters discovered in our laboratory that are expected to find value as nanoscale materials with unique properties. Research in our group is not only directed to elucidating the dynamical properties, structure, and stability of Met-Cars and related clusters, but also to producing and characterizing these in bulk quantities. Our interest in pure aluminum and aluminum alloy/compound clusters is related to the prospect of using these species as fuel additives or as new energetic materials. In addition to our focus on metal and metal containing clusters, hydrogen bonded and van der Waals clusters also are studied in order to lay the foundation for a more complete understanding of the interaction of these clusters with intense pulses of femtosecond laser radiation, partly to further develop the Coulomb explosion technique we devised for interrogating intermediates in fast reactions, but also to help develop techniques for studying fast reactions of isolated and cluster bound organic molecules for assessing the effectiveness of selected nanoscale catalysts.

II. Brief Summary of Accomplishments:

As one phase of our recent program, we undertook studies to determine accurate values of the ionization potentials of Met-Cars. Attention was directed to determining the shapes of the threshold functions for the titanium and zirconium systems. The findings are of value in furthering knowledge of the electronic properties, but also in order to understand their structures. Particular attention continued to be focused on both the pure-metal and mixed-metal Met-Cars of the stoichiometry $\text{Ti}_{8-x}\text{Zr}_x\text{C}_{12}$ ($x = 0-4, 8$) since these are species where there have been particular discrepancies with the literature values. As discussed below, knowledge of their IP's is also important to unravel the unique observed delayed ionization of these species. In addition, comparison between theoretically predicted and experimentally measured IP's provides a good test for both types of investigation, which hence bridges the gap between theoretically constructed pictures of Met-Cars and experimental observations.

The instrument used in these studies was a time-of-flight mass spectrometer coupled with a laser-induced plasma reactor as a cluster source, and a dye laser for photoionization. Experiments were conducted under conditions of sufficiently high powers of the ablation laser for cluster formation, so that neutral Met-Cars were produced abundantly among other neutral species. To obtain the IP's at higher precision, we measured the near-threshold photoionization efficiencies of the Met-Cars over a wide range of photon energy.

Study of the photoionization efficiencies of these species at different photon energies led to a determination that the IP's for the titanium and zirconium Met-Cars, Ti_8C_{12} and Zr_8C_{12} , are 4.40 ± 0.02 and 3.95 ± 0.02 eV, respectively. The IP's for the binary metal Met-Cars, $\text{Ti}_{8-x}\text{Zr}_x\text{C}_{12}$ ($x = 1-4$), were also determined, and it was found that the IP decreases continuously from that of the pure titanium Met-Car toward that of the pure zirconium Met-Car as the number of substituting zirconium atoms increases.

Prior to these investigations in our group of the IP's of the Met-Cars, there was an experimental study by Brock and Duncan in which similar near-threshold photoionization techniques were utilized to determine the IP's. They determined the IP's for the titanium and zirconium Met-Cars to be 4.9 and above 5.76 eV, respectively, which are significantly higher than our IP's. In order to explain the discrepancy between their and our IP's, during the past year we also conducted experiments in which effects of the temperatures of the clusters were investigated in detail. This was done since the IP's might tend to be assigned to a lower than actual value if a measurement is conducted at high temperatures. The experiments were accomplished with a newly built exit nozzle for our cluster source of which the temperature could be reduced from room temperature to liquid-nitrogen temperature. Importantly, at reduced temperatures, no significant shift to a higher value in IP assignments was observed. Therefore, it was concluded that there is no influence of the internal energy content of our clusters on the IP assignments. On the other hand, the reason why the IP's are significantly different between the two groups is still not certain. We speculate that, in the experiment by Brock and Duncan, some co-existing species may have disturbed their IP measurements.

The establishment of the IP values provided further basis for attributing the delayed ionization dynamics observed in Met-Cars to a thermionic emission mechanism. Two crucial parameters must be considered in accounting for this ionization mechanism, i.e. the IP's of the Met-Cars and their bond strength. The bond energies were previously estimated to be about 9 eV based on collision-induced dissociation experiments conducted in our group. Our determination of the IP's (ca. 4 eV) made it clear that the Met-Cars satisfy the criterion for the delayed ionization, i.e. the bond energy of an ionizing species must be considerably higher than its IP. In addition, it should be noted that our estimation of the IP's by parametrization based on the thermionic emission model of the experimental data for the delayed ionization led us to comparable values with the ones directly measured here.

The IP's of the titanium and zirconium Met-Cars determined in these studies were compared with the theoretically predicted IP's. The IP's were calculated by several groups employing density functional calculations of various levels. A most intriguing finding by the calculations is that the IP's were predicted to be significantly different for different proposed structures: For example, the IP was predicted to be equal to or *greater* than 5.3 eV for the T_h -symmetry titanium Met-Car whereas it has been predicted to be equal to or *less* than 4.7 eV for the T_d -symmetry titanium Met-Car. A similar trend was also found for the zirconium Met-Car. The experimentally determined IP's agree quite well with the calculated IP's when T_d symmetry is imposed. If the density functional calculations are assumed to be of high quality for estimating the IP's of the clusters studied here, the experimentally obtained IP's would suggest that the T_d -symmetry Met-Cars are present in considerable amounts and hence that they have high stability.

A thorough experimental and theoretical investigation into the observed delayed ionization, after excitation with a nanosecond pulsed laser, in both single and binary metal Met-Cars was completed and the results were published. (See publication 460 listed below.) Delayed ionization was observed in all Met-Car systems studied and, in the case of the single metal Met-Cars, it was found that the rate of delayed ionization is dependent on the type of metal incorporated into the cluster. In the case of the mixed metal, or binary metal, Met-Cars, a non-monotonic dependence was found with respect to the degree of metal substitution. The experimental results were modeled using Klotz' formalism for the treatment of electron emission from small particles. Variable temperature experiments were performed in order to determine a reasonable value for the initial cluster temperature used in the modeling. Using the photoabsorption cross section as the only initial adjustable parameter, the model predictions correspond very well with the experimental results, when the experimentally measured ionization potentials are applied to the model. For systems where the ionization potential has not yet been measured, the thermionic emission model can be used to predict the unknown ionization potential, by adjusting the IP value in the model until agreement with experimental data is achieved. In addition, during the grant period we performed additional experiments over a wide range of excitation wavelengths in order to determine if the observed delayed ionization is due to a specific long lived (triplet) state, or if the delayed ionization is truly the nanoscale equivalent of bulk phase thermionic emission, and therefore not attributable to any specific molecular state. It was found that the delayed ionization model predicted the experimental trends observed with changing excitation wavelength.

Delayed atomic ion emission, previously observed in the single-metal Met-Cars systems, is also observed in the binary metal Met-Cars. To the best of our knowledge, delayed atomic ion emission has not been observed in any other cluster system. In order to further investigate this unique phenomena, our experimental apparatus has been extensively modified in order to perform a "negative ion, neutralization, positive ion" (NeNePo) experiment. Briefly, a distribution of negative ions is produced in a laser vaporization source coupled to a time-of-flight mass spectrometer. The species of interest is mass selected from the distribution and then is neutralized via photodetachment of the excess electron; this produces a beam of mass selected neutral clusters. The neutral species can then be interrogated without possible interference from other clusters in the distribution. This technique is being implemented to study the delayed atomic ion emission, observed in Met-Car systems.

We have focused considerable effort on producing Met-Cars in macroscopic quantities and then isolating the desired species from the soot matrix in which it is embedded. Previously, we have shown that Met-Cars can be formed via arc-discharge (1), the direct laser vaporization (DLV) of metal carbides (see publication 454), and more recently using DLV of metal/fullerene mixtures (2). Met-Car containing soot is produced from laser vaporization of various metal carbides (TiC, ZrC, VC, and NbC) in an argon atmosphere inside a modified Erlenmeyer flask (Inert Gas Erlenmeyer, IGE). These soots can be extracted using various solvents, either by a batch or Soxhlet method. Analysis is performed on both the soot and extracted solutions. Solid state analysis of soot produced in the IGE have been performed using various techniques. Such techniques include: laser desorption time-of-flight mass spectrometry (LD TOF-MS), scanning tunneling microscopy (STM), and ^{13}C nuclear magnetic resonance (NMR). Analysis of Soxhlet extracted material includes: Uv-vis spectroscopy, transition metal ($^{45,47}\text{Ti}$, ^{91}Zr , ^{51}V , and ^{93}Nb) NMR, and , STM. Preliminary STM images had been taken with Zr-Met-Car containing soot deposited onto a gold substrate using a mass selected ion beam. STM images of the depositions showed structures near spherical, corresponding in radius to that expected for the Met-Cars.

More recently we have examined extract solutions dried onto surfaces using STM. This was accomplished by dropping a small amount of a methanol batch extraction onto substrates, drying them under vacuum and imaging the particles that remain. We found a number of

spherical structures on a MoS_2 (molybdenite) that correspond in size to that of the Met-Car species. There were a number of other particles which could be moved under low tip voltage conditions leaving only the Met-Car species on the surface. Suitable images on MoS_2 were obtainable for currents in the range of 20 pA to 1 nA and for voltages between 100 - 500 mV. In order to do spectroscopy we needed to move to a different substrate. We then imaged material deposited on gold and 2-mercaptoethylamine (MEA)-modified gold **Figure 1**. We first attempted to perform an current-voltage (I-V) study on the Met-Cars on the plain gold surface but the Met-Car moved under the influence of the STM tip, we then moved to the MEA-modified gold substrate. The terminal amine on the MEA-modified gold should hold the Met-Car in place during an I-V experiment, but the Met-Car still moved to some extent under the influence of the tip at higher voltages. Thus far we have only been able to obtain half of an I-V curve, but future studies at low temperature should aid in obtaining the full I-V curve. A more detailed explanation of the experiment can be found in a publication submitted to the *Journal of Nanoparticle Research* (3).



Figure 1. Met-Car on MEA-modified gold. Sample imaged at bias voltage +400 mV, current 1.0 nA.

The new apparatus built to produce and then directly analyze Met-Cars may be operated in a variety of modes: laser desorption (LD), direct laser vaporization (DLV), and thermal desorption (TD). In order to perform LD or DLV analysis, a sample crucible is placed just below the TOF lenses where the laser can be loosely focused to perform LD analysis on a material in the crucible or focused tighter, with increased power to perform DLV of materials. With one laser performing the LD or DLV we can examine the ions produced, using pulsed TOF lenses. With the addition of a second laser, we can also examine any neutrals produced in either a LD or DLV experiment via multiphoton ionization (MPI). For TD experiments a sample filled crucible is resistively heated in a tungsten basket, with the desorbed neutral species observed via MPI ionization. The overall greater flexibility gained by the implementation of this new DLV/LD/TD TOF-MS will allow us to greatly expand our current efforts at producing and isolating the various Met-Car species.

Using the DLV mode of the TOF-MS we have been able to produce Met-Cars from a mixture of zirconium (Zr) and fullerene powders, showing this to be an effective way of producing these species. This represents an extension of the fullerene-coated studies performed in molecular beams (4). LD and TD experiments of the Zr/fullerene mixture show only the fullerene distribution. As we increase the laser power, however, we can see the Met-Car species grow in and then dominate the spectra **Figure 2**. These studies show give us insight into the formation dynamics of the Met-Cars and the importance of C_2 units in the building pattern.

Our results show promise that these new materials can be produced, isolated, and

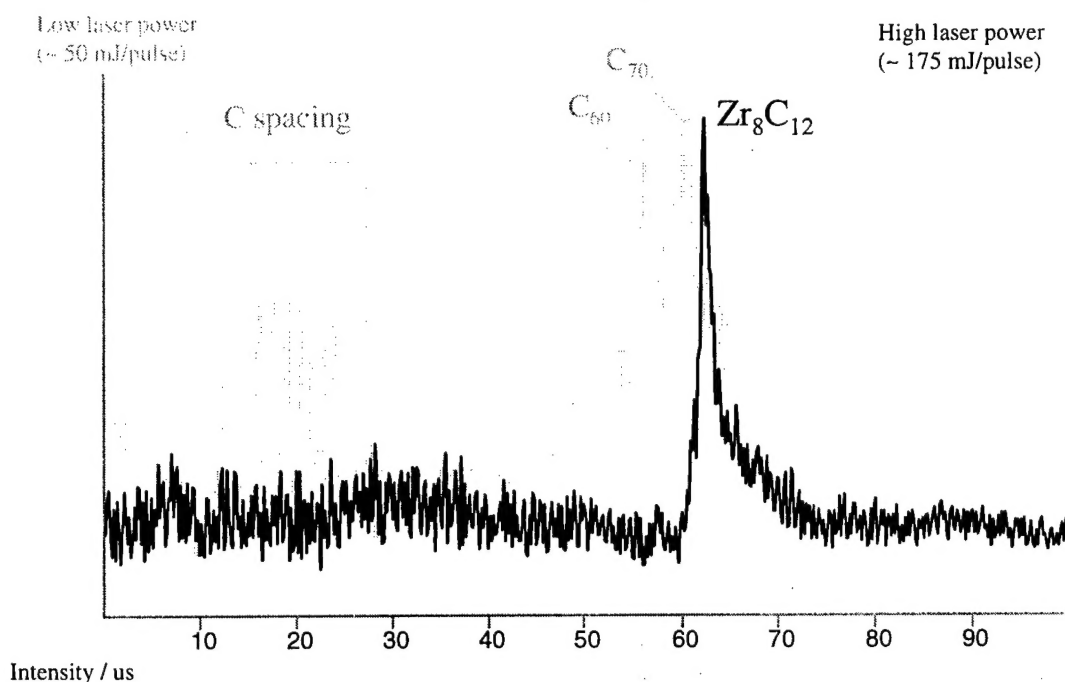


Figure 2. DLV of Zr/fullerene powder mixture at two laser powers.

characterized. The STM imaging of Met-Cars on modified gold, needs to be performed at lower temperatures in order to perform informative spectroscopies. Performing extractions with various solvents will allow us to identify a solvent that is able to solublize greater amounts of Met-Cars which would facilitate characterization. In addition, a higher concentration of Met-Cars in the soot would greatly enhance any attempts to isolate and characterize these species which may be accomplished via the DLV of metal/fullerene mixtures in the IGE. The new DLV/LD/TD TOF-MS combines greater experimental control during the DLV event, so that Met-Car concentration may be maximized in the soot. This new multi-functional TOF-MS has been shown to perform in all three modes (DLV, LD, and TD) and has demonstrated a novel method of Met-Car production. We expect the combination of these techniques will allow us to eventually fully characterize these unique molecular species.

During the grant period we also have been developing new methods of studying the dynamics of molecular clusters for eventual use in studies of the dynamics of Met-Car reactions. In order to demonstrate the applicability of Coulomb explosion as a method of unraveling the intermediates in a fast reaction, we have performed a series of experiments on the model DNA base pair 7-azaindole (5). Investigations were undertaken by our group to further elucidate the nature of the ultraviolet light induced double proton transfer exhibited by the dimer of this species (6). In addition to the time dynamics data obtained, these investigations have led us to develop a new method for investigating ultrafast reactions. In order to overcome questions which have arisen regarding the interpretation of biexponential transients, we developed a new way to monitor ultrafast reactions using Coulomb explosion such that the intermediate species are directly monitored. (See publication 465.) This technique offers advantages over traditional optical transient methods in that it does not require differences in the ionization cross-sections of the reacting species; rather it is based upon the observation of actual fragments formed during the course of a reaction.

In these studies, the 7-azaindole dimer is formed in a molecular beam, ionized with a femtosecond laser, and then analyzed with a time-of-flight mass spectrometer. Specifically, a weak pump UV photon impinges upon the neutral dimer and initiates the proton transfer. The excited dimer species is then Coulomb exploded with a time-delayed strong probe laser beam. The Coulomb explosion effectively halts the reaction by rapidly breaking the dimer apart into two monomer units. Depending on the progress of the proton transfer reaction before the Coulomb explosion, the separated monomer units will either have the same mass, or a mass differing by two due to the loss and gain of a proton by the respective species. In this way we were able to verify that 7-azaindole undergoes a stepwise rather than a concerted double proton transfer by observing the appearance and disappearance of a protonated monomer unit. Thus by mass spectrometrically identifying the intermediate species in the tautomerization process of 7-azaindole we were able to contribute new chemical information which gives further insight into the findings of a prototypical biologically interesting molecule.

During the course of studying ionization and concomitant Coulomb explosion, we conducted experiments with femtosecond laser pulses of several mJ energy. When focused to a power in excess of 10^{14} W/cm², they produce intense electric fields, with the amplitude of the electromagnetic waves exceeding 3 V/Å. This field is comparable with that which binds valence electrons in molecules. Atoms, molecules, and clusters, when exposed to laser pulses at such intensity, can be highly ionized, producing atomic fragment ions with various kinetic energies due to the strong Coulomb repulsion between the high charges. Average kinetic energy release of several hundreds to thousands has been observed for small van der Waals and hydrogen bonded clusters in our laboratory (7,8). (Also see publication 469.) Interestingly, in one of our recent experiments, the atomic iodine ions generated from multielectron ionization of methyl iodide clusters by 100 fs laser pulses at 400 nm with $\sim 10^{15}$ W/cm², are observed to experience secondary electron loss by passing through the close vicinity of the nickel meshes mounted on the Time-of-Flight acceleration and ground lenses. All the cluster ions are not observed to go through any further ionization. Experimental evidence shows that these iodine ions are actually highly excited Rydberg ions, which are produced during the later stage of the ionization process through interactions with electrons and/or UV/x-ray photons generated during the multielectron ionization event. The excited atomic iodine ions are readily ionized by the high electric field in close proximity to the nickel meshes. The formation of these highly excited Rydberg ions in many-electron multiphoton-ionization events is another valuable findings in efforts to understand the mechanism of this multielectron ionization process.

Photoionization studies of cluster systems are often complicated by fragmentation of initial parent clusters upon ionization. Often higher mass clusters may dissociate upon ionization and "feed down" into lower mass clusters; this effect can be especially predominate when using non-resonant above threshold ionization. Most experimental methods commonly employed to study the photoionization of cluster systems are unable to probe the possible initial fragmentation events. We have developed a technique to investigate these typically unseen fragmentation processes that also provides insight into cluster formation / building processes, namely covariance and correlation coefficient mapping.

We previously employed this covariance mapping technique to gain insight into the Coulomb explosion process using ammonia clusters as a test case. Now, we have expanded our covariance mapping studies to investigate formation and dissociation processes in titanium-carbon clusters, including the titanium Met-Car. Although the titanium-carbon cluster system is quite complicated, the covariance mapping technique has provided important information about the connections between different clusters. For

example, a strong anti-correlation is noted between TiO^+ and Ti_2C_4^+ , Ti_2C_2^+ , TiC_4^+ , TiC_2^+ , TiC^+ , and Ti^+ . This observation qualitatively agrees with previous experimental results that show when intense titanium oxide peaks are present in the mass spectrum, it is difficult to produce larger titanium-carbon clusters and if the titanium oxide peak is intense enough, the titanium Met-Car will not be produced. In addition, a strong anti-correlation between TiC_2^+ , the main building block of the titanium Met-Car, and C^+ , CH_3^+ , and CH_4^+ was determined. This observation is also consistent with previous studies in our group that determined the total dehydrogenation of the starting hydrocarbon gas is critical in the production of high mass titanium-carbon clusters, specifically the Met-Cars. (See publication #480)

In addition to our new covariance mapping studies of Met-Cars, we undertook a collaboration with Prof. Gerber's group at the Universität Würzburg, on the multiphoton photoemission from supported metal-carbon / Met-Car clusters. Zirconium Met-Cars were produced at Penn State using our arc discharge apparatus, and a dilute solution of material was extracted in methanol. To deposit the material on a substrate, this dilute solution was evaporated on the substrate of choice. A UHV-STM was used to determine the topography of the substrate after evaporation and small bumps that can be identified as single molecules of a size indicative of Met-Car clusters can be observed.

Femtosecond multiphoton photoemission and time-resolved two-color two-photon photoemission spectroscopy of these metal-carbon clusters supported on graphite were investigated. Femtosecond laser pulses at 400 nm and 267 nm were used in the multiphoton photoemission studies. When 267 nm was used, the excitation spectra observed from a Met-Car sample had a different shape when compared to those obtained from graphite or from a graphite substrate on which pure methanol was evaporated. However, when 400 nm light is used, the excitation spectra from all three samples have the same shape. Therefore, it is concluded that at 267 nm excitation a resonant process in the adsorbed clusters is responsible for the change in shape of the two-photon photoemission spectrum. Preliminary time resolved measurements reveal a long lived electronic state with a lifetime of several picoseconds that is excited by 267 nm. Further studies are ongoing.

In separate experiments we have also further refined and confirmed our ionization potential measurements of the Met-Car systems. One question that arises when determining the ionization potentials of metal containing clusters produced in a laser vaporization source is how does the source / formation temperature affect the measured ionization potential? In order to answer this important question, we modified one of our laser vaporization sources to allow for cooling of the source and measured the ionization potential of Met-Cars at different source temperatures. It was observed that the ionization potential of the neutral Met-Car clusters did not noticeably change as the source temperature was reduced from room temperature to -190°C . While this study provided proof that the cluster source produces internally cool under operation at room temperature (due to adiabatic expansion from the high pressure region of the source to the high vacuum conditions of the mass spectrometer) and confirmed our previous ionization potential measurements, it also yielded additional insight. As the temperature of the source was lowered, the adsorption of intact methane molecules, present in the expansion gas, onto neutral Met-Car clusters was observed. This observation again confirms the stability of neutral Met-Car clusters, eliminating the possibility that, in this experiment,

the Met-Car clusters are formed via the fragmentation of larger metal-carbon clusters upon photoionization. (See publication 489)

Our new ultrafast laser system, purchased with funds from a DURIP grant, was installed and characterized and preliminary experiments are currently being performed. The new laser system is capable of producing sub 40 fs pulses and includes an OPA that covers the wavelength range from 220 nm to 3 μm . This new laser system has been coupled to a recently rebuilt and modified reflectron time-of-flight mass spectrometer, with increased resolution and mass range capabilities. Two color pump-probe experiments can now be performed over the entire range of wavelengths produced by the OPA, making the new system an extremely powerful and unique apparatus to investigate the electron relaxation dynamics in metal and metal containing clusters, as well as to conduct experiments pertaining to catalysis in the future.

One of the major activities during the first part of the last year involved making a full characterization of the optical pulses from our ultrafast femtosecond laser system acquired through DURIP funding, and undertaking requisite reconfigurations to obtain desired pulse widths and energies. We employed the laser system to first restudy a number of well characterized systems including the photophysics of methyl iodide and acetone. Characterization of ultrafast pulses is required for proper analysis and is necessary to ensure accurate interpretation of electronic lifetimes. Numerous modifications were made to the system during the course of these measurements. Thereafter, we commenced the proposed work on the studying electron relaxation dynamics, with specific emphasis placed on elucidating the collective electronic effects in Met-Car clusters.

During recent months, the excited state dynamics in vanadium-carbon clusters has been investigated via the femtosecond laser pump-probe technique, employing pulses at 620 nm and 400nm. These measurements represent the first time-resolved measurements of the electronic relaxation dynamics in such vanadium-carbon clusters including the vanadium Met-Car, V_8C_{12} . Significant size dependent trends were observed in the pump-probe transients that are suggestive of more extensive free electron character in larger clusters compared to the smaller clusters. The pump-probe transient of the vanadium Met-Car is illustrated in **Figure 3**. Measurements of the ionization potential of V_8C_{12} indicate that one 400 nm photon

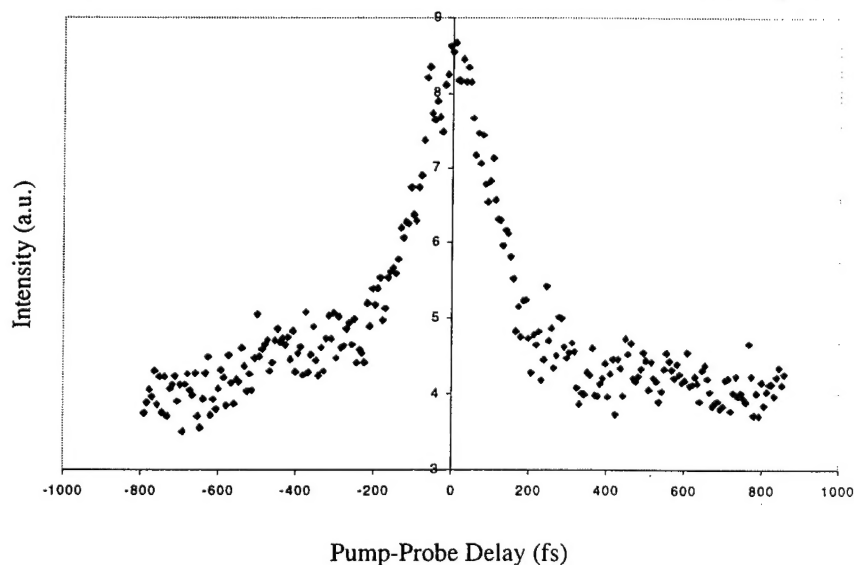


Figure 3. Pump-probe transient (pump: 400 nm, 50 fs, 24 μJ ; probe: 620 nm, 50 fs, 20 μJ) observed for the vanadium Met-Car cluster between delay times of -1 ps and +1 ps.

and one 620 nm photon is sufficient to exceed the IP.

The cross-correlation of the 400 nm pump and 620 nm probe beams is approximately 86 fs while the observed response of the V_8C_{12} cluster is 225 fs (FWHM). This distinct difference indicates that a state (or band of states) with an appreciable lifetime is being accessed. The fact that the Met-Car response is noticeably longer than the autocorrelation and that these clusters are strongly bound, also provides strong evidence that the pump-probe response is too short to be attributable to a fragmentation process, either in the Met-Car cluster itself, or fragmentation of a larger cluster to form the Met-Car. The pump-probe response is thus a measurement of electronic relaxation. At first glance the pump-probe transients for all of the observed vanadium-carbon clusters with more than four metal atoms appear to show a somewhat similar pump-probe response, as seen in **Figure 4**, with exponential decays on the order of a few hundred femtoseconds. This result suggests that the band of states accessed in the vanadium Met-Car is already present in clusters as small as the V_4C_x series.

Significantly, upon closer inspection and curve fitting, a progressive trend is noticed in the observed transients for V_4C_6 , V_5C_8 , V_6C_8 , V_7C_{12} , and V_8C_{12} ; see **Figure 5**. The experimental data were fitted using a typical least squares fitting method. Several trends are observable in the fitted and normalized transients. First of all, a narrowing of the transient is observed with increasing cluster size. This is suggestive of the expected increased free electron character with increasing cluster size. Secondly, the maximums of the fitted transients shift to longer delay times with increasing cluster size as would be expected for the initial onset of a delayed ionization process. Finally, the V_4C_6 and V_5C_8 transients exhibit a single exponential decay, while the V_6C_8 , V_7C_{12} , and V_8C_{12} transients display double exponential decays. The V_7C_{12} and V_8C_{12} clusters have almost identical fitted transients with one fast decay component and one longer, several hundred femtosecond, decay again suggestive of the initial onset of thermionic emission. The two color pump-probe transient shows an asymmetric response, significantly longer than the cross correlation of the pump and probe beams, indicative of excitation into different bands. Future studies will extend the study to investigate wavelength and fluence effects on the relaxation dynamics observed in not only the Met-Car cluster, but in other clusters of the distribution as well. The findings to date show a pronounced difference in the observed excited state dynamics, in the small (i.e. less than three metal atoms) clusters, while the clusters containing four or more vanadium atoms exhibit

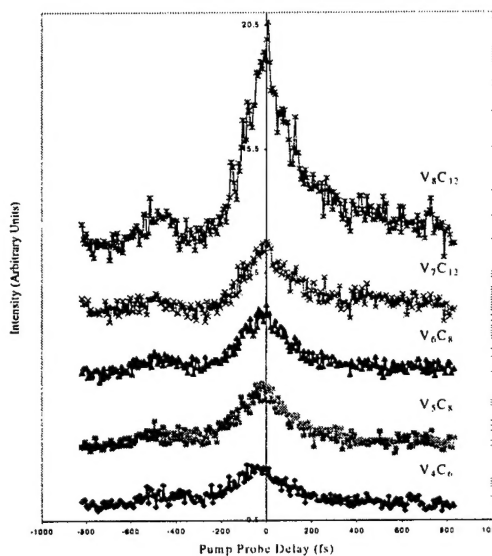


Figure 4. Pump-probe transients (pump: 400 nm, 50 fs, 24 μ J; probe: 620 nm, 50 fs, 20 μ J) observed for the vanadium-carbon clusters: V_4C_6 , V_5C_8 , V_6C_8 , V_7C_{12} , and V_8C_{12} between delay times of -1 ps and +1 ps.

similar pump-probe response. The pump-probe response is observed to narrow as the cluster size increases. This result suggests that the larger clusters have more free electron character and therefore the rate of energy relaxation is higher in the larger clusters. These new results provide important baseline data that can be used to test theoretical models addressing relaxation behavior in a wide range of metallic-like cluster systems that are expected to be increasingly encountered in the field of nanotechnology. It is worth noting that we also observed interesting oscillations in the pump-probe transients for clusters to which some hydrogen remained bonded, and these clearly warrant further study as these species are the precursors in the dehydration process responsible for Met-Car formation.

Other recent investigations exploring the electronic excitation and relaxation properties of the vanadium Met-Car also have been undertaken using shorter laser pulses. The data (see **Figure 6**) reveal vibrational frequencies in the ionization dynamics. Clear evidence for electronic energy to lattice coupling modes have been acquired with findings that the latter leads to the thermionic emission at long times as we have observed.

Currently we are undertaking pump-probe experiments on titanium Met-Cars to investigate the excited state/electron dynamics in these clusters for comparison with the vanadium system described in the foregoing. Preliminary pump probe studies, under two

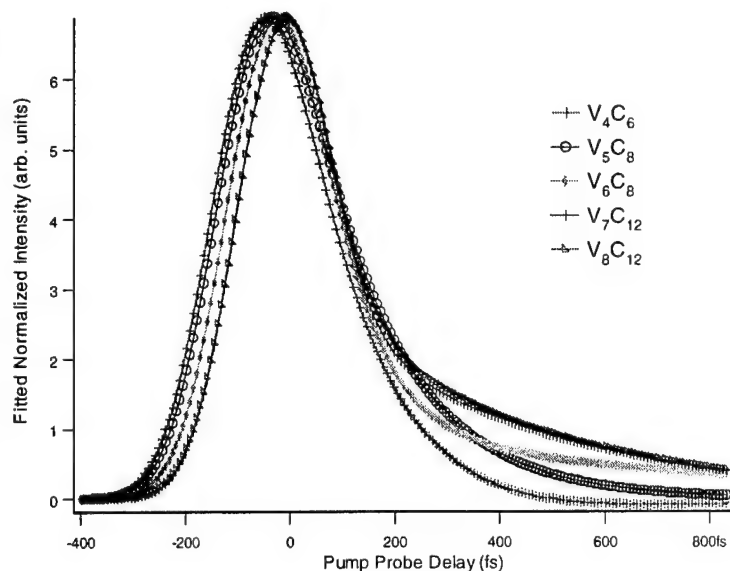


Figure 5. Summary of the fits of experimental pump-probe data for V_4C_6 , V_5C_8 , V_6C_8 , V_7C_{12} , and V_8C_{12} . Note that the transients become narrower with increasing cluster size and evolve from single to double exponential decay behavior.

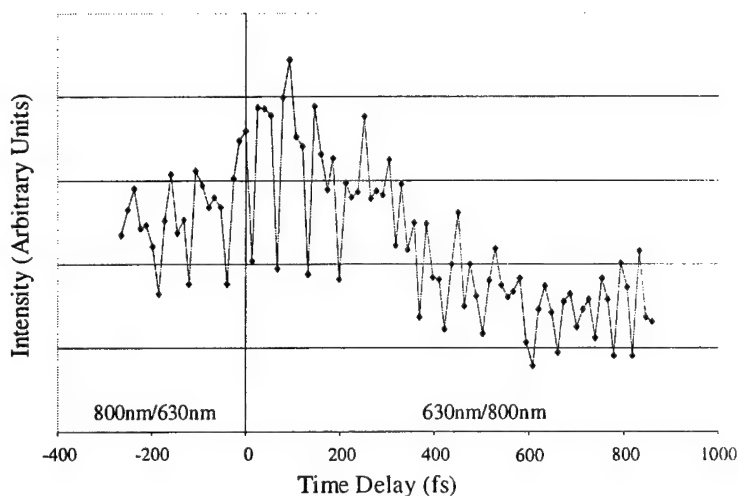


Figure 6. Pump probe transient observed for the V Met-Car, employing a 50fs, 620nm pump and 800nm probe. Measured resonance: 505cm^{-1} , VC on V surface: 575cm^{-1} Ti_8C_{12} resonance: 520cm^{-1} Duncan & others; PRL 83, 4983 (1999)

color conditions, show a short excited state lifetime which agrees with the expected free electron nature in the Met-Cars as shown in the right side of **Figure 7**. The shoulder on the right side is suggestive of relaxation behavior expected for a system which displays delayed ionization. In contrast to the vanadium system, the pump pulses on the negative delay side of the figure are accessing an electronic band calculated for these Met-Cars.

The femtosecond facility has also been employed as a photoionization laser. Mass spectra obtained for typical distributions of titanium-carbon clusters formed from the photoionization of neutral

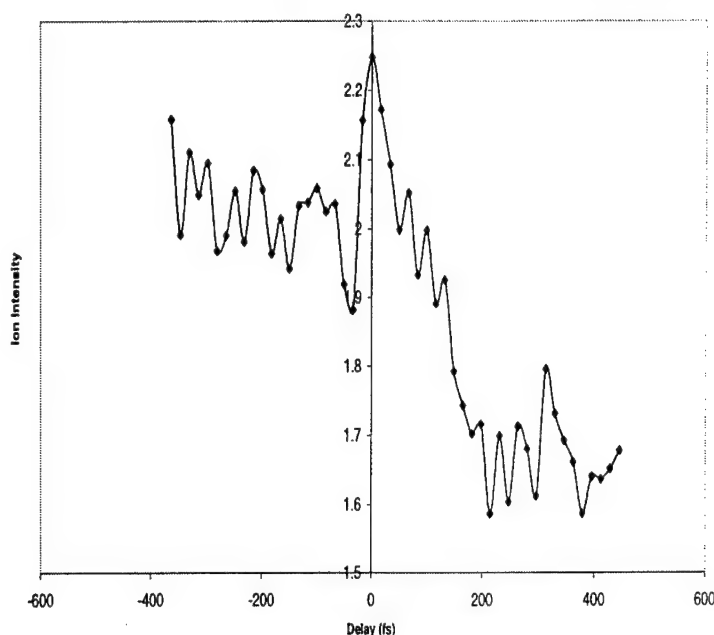


Figure 7. Pump probe transient observed for the Ti Met-Car, employing a 50 fs, 660 nm. pump and 400 nm probe.

species at 400 nm, 50 fs and 24 $\mu\text{J}/\text{pulse}$ were found to be almost identical to ones observed under photoionization with a 355 nm, 10 ns Nd:YAG pulse with one significant difference. Although the overall distribution did not change substantially, the "tailing" of the titanium Met-Car peak to higher mass, present in the nanosecond ionization case was found to be reduced or absent in the femtosecond photoionization spectrum acquired at this wavelength and fluence. The "tailing" of peaks to higher mass is indicative of delayed ionization. When short excitation pulses of very high fluence are employed, we find that direct multiphoton ionization dominates. Studies are currently underway to determine the combination of fluences, pulse widths, and excitation frequencies necessary to again give rise to the delayed ionization phenomenon. These studies will provide further insight into the electron relaxation rates in transition metal - carbon clusters, with particular attention to the excitation of various electronic bands. Evidently, in order to observe delayed ionization, energy has to be deposited into bands in a cluster system on a time scale that is longer than the energy redistribution time.

Photoionization studies of cluster systems are often complicated by fragmentation of initial parent clusters upon ionization. Higher mass clusters may dissociate upon ionization and "feed down" into lower mass clusters and this effect can be especially predominate when using non-resonant above threshold ionization. Most experimental methods commonly employed to study the photoionization of cluster systems are unable to probe the possible initial fragmentation events. We developed a technique to investigate these fragmentation processes, a technique that also provides insight into cluster formation / building processes; it is termed covariance and correlation coefficient mapping as discussed above.

In studies conducted during this past year, covariance mapping continues to be a useful technique for obtaining information about the connections between different clusters. For example, a strong anti-correlation has been found between TiCH_4^+ and various Met-Car building blocks including Ti_2C_4^+ , Ti_2C_2^+ , and TiC_2^+ . This observation is in accord with previous experimental results that show when intense titanium-methane species are present in the beam, sufficient dehydration to produce Met-Cars has not taken place. These observations provide further evidence for the mechanism of their formation in the plasma reactor. In addition, a strong anti-correlation between TiC_2^+ , the main building block of the titanium Met-Car, and C^+ and CH_3^+ was determined. This observation is also consistent with previous studies in our group that determined the total dehydrogenation of the starting hydrocarbon gas is critical in the production of high mass titanium-carbon clusters, specifically the Met-Cars.

A study of the gas phase reactions of aluminum and aluminum clusters with a variety of reactants continued, with emphasis on identifying systems that may be suitable for storing aluminum for use as a fuel additive. Work on reactions with chlorine and nitrogen oxides showed the appearance of magic numbers that provide further evidence for the composite Jellium model which we proposed to account for our findings on aluminum-carbon clusters. Our work has raised interest among various theoretical groups and S. Khanna at the Virginia Commonwealth University is undertaking theoretical calculations in support of our experimental findings. Concurrent to our studies of transition metal-carbon clusters, we have also obtained important new information about aluminum containing clusters. Aluminum and aluminum containing clusters show promise for use in the formation of new materials through cluster assembly techniques. As has been reported previously, Al_{13}^- , Al_{23}^- , and Al_{37}^- all show unique stability, and correspond to shell closures in the Jellium model. Recently, we have investigated aluminum-carbon cluster anions, specifically looking for clusters that also

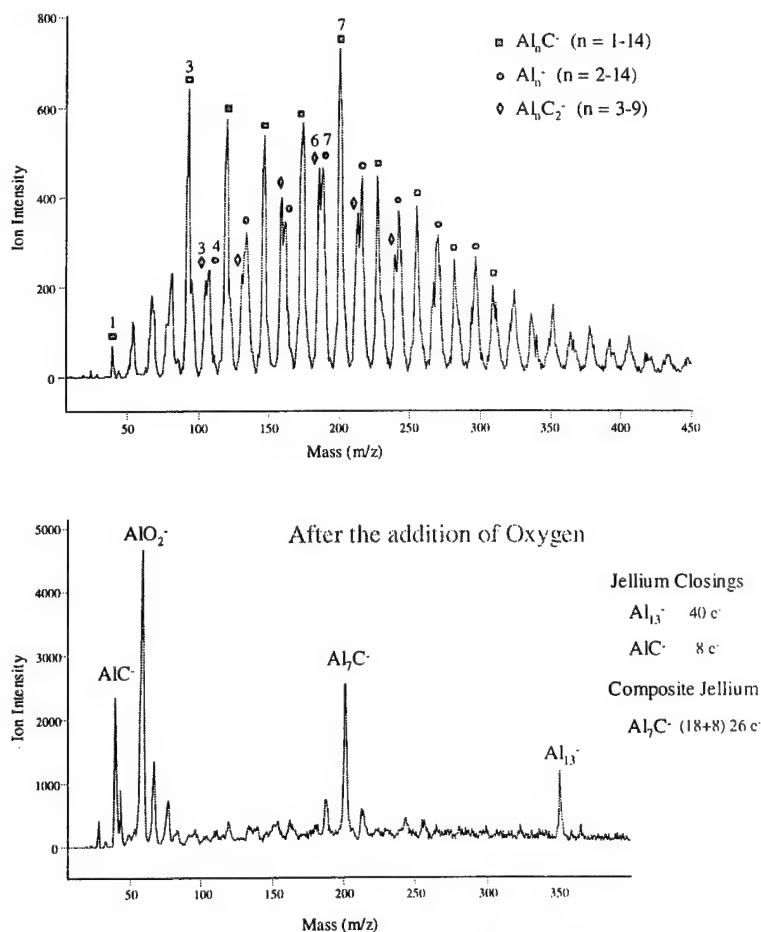


Figure 8. Aluminum and aluminum-carbide distribution before and after the addition of oxygen. Note the enhanced stability of AlC^- and Al_7C^- in the presence of oxygen.

demonstrate unique stability due to shell closure effects.

A study of the gas phase reactions of aluminum-carbon clusters with oxygen under well-defined thermal conditions has been completed. Aluminum-carbon cluster anions were formed and introduced into a flow reactor where they were reacted with oxygen. A relative increase in the abundance of species of unique stability is observed and is accounted for in terms of the etching of higher order species that then feed down into smaller clusters of high stability. In these sets of experiments, AlC^- and Al_7C^- were observed to be especially stable (see **Figure 8**). The observed stability of AlC^- can be explained by the propensity of carbon to fill its 2p valence shell. The carbon atom may effectively use the overall charge on the cluster and the three valence electrons of the aluminum to gain its stability. The observed stability of Al_7C^- can be explained in a similar manner. Carbon

requires four additional electrons to fill its outer 2p shell and may utilize three electrons from an aluminum atom and the additional electron from the overall charge of the cluster. With four valence electrons now filling the carbon 2p shell, the remaining 18 valence electrons allow for a very stable aluminum species. (See publication 495). At the present time, findings suggest the aluminum-carbon complexes to be the most promising ones with which to begin exploring the production of the bulk nanoscale materials. Also, the prospect of storing these stable anionic aluminum and aluminum carbide clusters in combination with an organic cation of high energy content, such as $C_3(CH_3)_3^+$, is particularly intriguing. We plan to commence this project upon acquiring and installing new equipment from the Intel Corporation which is expected to be suitable for producing deposited nanoscale cluster materials.

As a further contribution toward developing concepts for producing cluster assembled materials of desired properties, we are also undertaking investigations of the formation and growth of silicon and silicon oxide clusters. Note, from the various

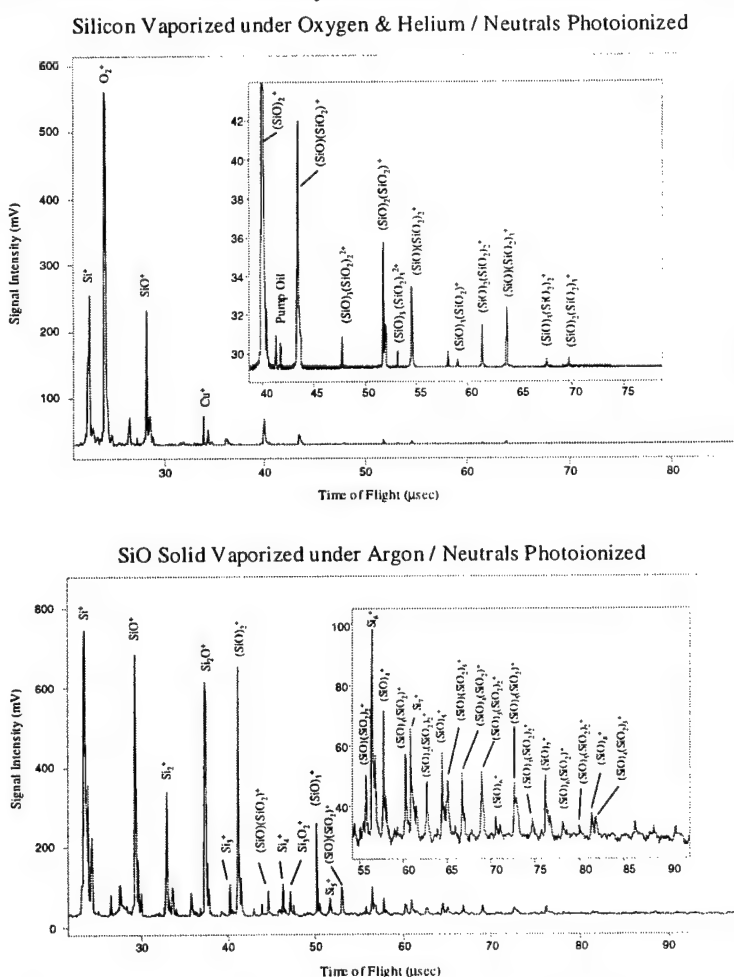


Figure 9. Neutral silicon clusters vaporized with 50fs, 800nm light.

experiments conducted to date, SiO appears to be the core about which the growth of the oxides proceeds (see **Figures 9 & 10**). SiO_2^+ is only seen as a minor cation, but not observed as a neutral molecule until initial cluster growth has commenced.

In addition to our studies of strongly bound molecular / metallic clusters, we have continued our investigations of hydrogen bonded and van der Waals clusters, being undertaken to further develop our understanding of cluster phenomena. In particular, we have concentrated on the interaction of intense pulses of femtosecond laser pulses with these clusters, typically observing Coulomb explosion processes. In a study of the Coulomb explosion of methyl iodide clusters at 795 nm, the

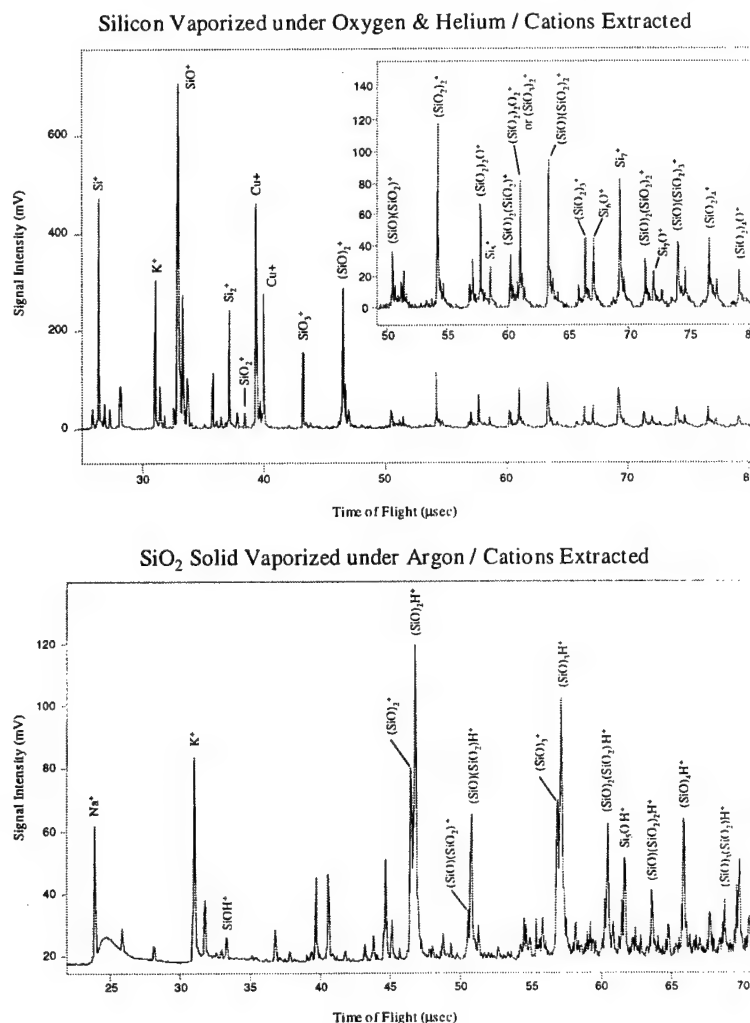


Figure 10. Cationic silicon cluster distribution. Note the presence of SiO_2^+ monomer.

effects of different carrier gases, laser power, cluster distributions, and the resulting Coulomb explosion energies were examined. A major finding of the study was that clusters must be present in the distribution in order to see an appreciable amount of Coulomb explosion products. There are two major theoretical models typically used to describe the Coulomb explosion process, namely the Ionization Ignition Model (IIM) and the Coherent Electron Motion Model (CEMM). Our new studies support aspects of both models, suggesting that the true mechanism of Coulomb explosion process is not yet completely understood and may involve parts of both models. The new experimental results should stimulate further theoretical investigations into this intriguing topic.

Coulomb explosion processes induced by intense femtosecond laser pulses in clusters, release energies on the order of several hundred electronvolts. We performed molecular dynamics simulations of the Coulomb explosion process on the level of pure electrostatic interactions between the ion cores formed in the event. The calculations again show that clusters are critical to the Coulomb explosion process. The energies observed being released in the process can not be explained by Coulomb interactions

between highly charged ion cores within a single molecule. However, when small to medium sized clusters are considered, the energies observed can be accounted for by simple direct Coulomb interactions between the charged ions produced. The simple molecular dynamics simulation performed has proven to provide physical insight into the Coulomb explosion process in clusters.

As a prelude to work on ligated clusters of interest in catalysis, the Coulomb explosion technique was employed to investigate water solvated 7-azaindole (also of interest in the context of a model DNA base pair.). This study has further elucidated the nature of the reactive and non-reactive dimers and establishes that the excited state double proton transfer occurs in a stepwise rather than a concerted manner. The study shows that when the non-reactive dimer is solvated, the addition of water can actually facilitate the proton transfer reaction, the non-solvated non-reactive dimer will not undergo proton transfer, but the solvated non-reactive dimer will.

Continuing effort was placed on resolving the many controversial issues surrounding the dynamics of 7-azaindole, with particular attention to the effect of hydration on the tautomerization of the dimer and monomer. The 7-azaindole dimer is capable of forming two distinct isomers in the gas phase depending upon the clustering expansion conditions employed and we showed that it is their conformation rather than clustering which governs their behavior following photoexcitation. In the new studies, hydrated clusters of the "nonreactive" 7-azaindole dimer were formed for complexes comprised of one to nine waters. Over the range of one to three waters, the double proton transfer was observed to occur in two distinct steps with time constants on the order of 600 femtoseconds for the first proton transfer and about two picoseconds for the second proton transfer. Upon the addition of four water molecules to the dimer, the double proton transfer began to occur in a single concerted step rather than in a stepwise fashion. In conjunction with theoretical studies, we conclude that upon the addition of four water molecules to the dimer, the hydrogen bonds stabilizing the dimer in a planar fashion are overcome, leading to a conformational change to a stacked dimer arrangement, with individually hydrated monomer species. This has been corroborated by experimental studies in our group on the hydrated monomer conducted during the last few months, which show that a concerted proton transfer takes place upon the addition of a critical number of water molecules. The waters serve to catalyze the reaction, enabling a proton transfer along a water wire connecting the donor and acceptor sites on the rings. These results can be understood by considering that in bulk water, 7-azaindole dimer species are not formed, but rather exist as hydrated 7-azaindole monomer species. In this respect we have been able to study the transition between the gas phase and the condensed phase for the hydrated 7-azaindole dimer by utilizing cluster chemistry techniques.

In addition to our studies of the femtochemistry of proton transfer in 7-azaindole, as a prelude to work on ligated clusters of interest in catalysis, the Coulomb explosion technique was employed to investigate this system, obtaining additional evidence for the role of clusters in facilitating the process. A detailed study of the effects of formation conditions, laser power, laser wavelength, and cluster distribution has been performed. The results support the dynamic CREI model set forth by Jortner and Bandruck and their coworkers. Employing the covariance technique discussed in last years report and analyzing the results in terms of the kinetic energy release in the phenomenon, we were

able to ascertain the differences in positive and negative correlation values as being attributable to competitive processes in the case of the latter while parallel processes are responsible for the former. These confirming experiments are of great value in interpreting the results of cluster experiments which can be plagued by severe fragmentation.

References:

1. S. F. Cartier, Z. Y. Chen, G. J. Walder, C. R. Sleppy, and A. W. Castleman, Jr., *Science*, **260**, 195, (1993).
2. B. J. Toleno, M. E. Lyn, and A. W. Castleman, Jr., in preparation.
3. G. S. McCarty, J. C. Love, J. G. Kushmerick, L. F. Charles, C. D. Keating, B. J. Toleno, M. E. Lyn, A. W. Castleman, Jr., M. J. Natan, and P. S. Weiss, *Journal of Nanoparticle Research*, **1**, submitted.
4. F. Tast, N. Malinowski, S. Frank, M. Heinebrodt, I. M. L. Billas, and T. P. Martin, *Phys. Rev. Lett.*, **77**, 3529, (1996).
5. D.E. Folmer, L. Poth, E.S. Wisniewski, A.W. Castleman, Jr., *Chem. Phys. Lett.* **287** (1998) 1.
6. A. Douhal, S.K. Kim, A.H. Zewail, *Nature* **378** (1995) 260.
7. E. M. Snyder, S. A. Buzza, A. W. Castleman, Jr. *Phys. Rev. Lett.* **77**, 3347-3350 (1996).
8. S. A. Buzza, E. M. Snyder, D. A. Card, D. E. Folmer, A. W. Castleman, Jr. *J. Chem. Phys.* **105**, 7425-7431 (1996).

Personnel Supported:

A. W. Castleman, Jr., Principal Investigator
Denis E. Bergeron, Ph.D. Student (Aasert)
Daniel Folmer, Ph.D. Student
Steven Kooi, Ph.D. Student
Dina R. Justes, Ph.D. Student (Aasert)
Margaret E. Lyn, Ph.D. Student
Lutz Poth, Postdoctoral Fellow (partial support)
Hiromu Sakurai, Ph.D. Student (partial support)
Jason Stairs, Ph.D. Student (Metallo)
Pavel Svilenov, Ph.D. Student (Metallo)
Brian Toleno, Ph.D. Student
Bob Wang, Ph.D. Student (Metallo)
Eric Wisniewski, Ph.D. Student (partial support)
Qun Zhong, Ph.D. Student (partial support)

IIIa. List of Publication Sponsored by AFOSR Since This Grant Commenced September 1, 1997.

440. "The Influence of Solvation on Ion-Molecule Reactions," A. W. Castleman, Jr., in *Advances in Gas Phase Ion Chemistry, Vol. 3* (L. M. Babcock and N. G. Adams, Eds.) JAI Press, Connecticut, pp 185-253, 1998.
453. "Titanium-Carbon Clusters: New Evidence for High Stability of Neutral Met-Cars," H. Sakurai and A. W. Castleman, Jr., *J. Phys. Chem.* **100**, 7695-7698 (1997).
454. "Metallocarbohedrenes: The Quest for New Materials," B. J. Toleno, H. Sakurai, S. E. Kooi, J. L. Baling, M. E. Lyn, and A. W. Castleman, Jr., *Proc. Ninth International Conference on High Temperature Materials Chemistry* (K. E. Spear, Ed.), Electrochemical Society, NJ, pp 637-647
460. "Delayed Ionization in Transition Metal-Carbon Clusters: Further Evidence for the Role of Thermionic Emission," S. E. Kooi and A. W. Castleman, Jr., *J. Chem. Phys.* **108**, 8864-8869 (1998).
461. "Molecular Dynamics Simulation of Coulomb Explosion Processes," L. Poth and A. W. Castleman, Jr., *J. Phys. Chem.* **102**, 4075-4081 (1998).
463. "Ionization Potentials for the Titanium, Zirconium, and Mixed Metal Met-Cars," H. Sakurai and A. W. Castleman, Jr., *J. Phys. Chem.*, **102**, 10486-10492 (1998).
465. "Arresting Intermediate States in a Chemical Reaction on a Femtosecond Time Scale: Proton Transfer in Model Base Pairs," D. E. Folmer, L. Poth, E. S. Wisniewski, and A. W. Castleman, Jr., *Chem. Phys. Lett.* **287**, 1-7 (1998).
469. "Charge Stripping Effects from Highly Charged Iodine Ions Formed from Coulomb Explosion of CH₃I Clusters," L. Poth, Q. Zhong, J. V. Ford, S. M. Hurley, and A. W. Castleman, Jr., *Chem. Phys.*, **239**, 309-316 (1998).
474. "Scanning Tunneling Microscopy and Spectroscopies of Nanometer-Scale Particles," G. S. McCarty, J. C. Love, J. G. Kushmerick, L. F. Charles, C. D. Keating, B. J. Toleno, M. E. Lyn, A. W. Castleman, Jr., M. J. Natan, and P. S. Weiss, *Journal of Nanoparticle Research*, **1** (4):459-466, (1999).
480. "The Interaction of Titanium-Carbon Cluster Fragments," D. A. Card, D. E. Folmer, S. Kooi, S. Sato, and A. W. Castleman, Jr., *European Journal of Physics D*, ISSPIC 9" 9/1-4, 195-200, (1999).
481. "Femtosecond Laser Interactions with Methyl Iodide Clusters: Part 1. Coulomb Explosion at 795 nm," J. V. Ford, Q. Zhong, L. Poth, and A. W. Castleman, Jr., *J. Chem. Phys.* **110**, 6257- (1999).
485. "Femtosecond Laser Interactions with Methyl Iodide Clusters: Part 2. Coulomb Explosion at 397 nm," J. V. Ford, L. Poth, Q. Zhong, and A. W. Castleman, Jr., *Int. J. Mass Spectrom. Ion Processes*, **192**, 327-345, (1999).
489. "Latest Findings on the Photoionization of Met-Cars," H. Sakurai, S. E. Kooi, and A. W. Castleman, Jr., *J. Cluster Science*, **10**, 493, (1999).
494. "Femtosecond Cluster Studies of the Solvated 7-Azaindole Excited State Double Proton Transfer," D. E. Folmer, E. S. Wisniewski, S. M. Hurley, and A. W. Castleman, Jr., *Proc. Natl. Acad. Sci.*, **38**, 5709-5715 (1999).

495. "The Interplay Between the Electronic Structure and Reactivity of Aluminum Clusters," B. D. Leskiw and A. W. Castleman, Jr., *Chem. Phys. Lett.*, **315**, 49-54 (1999).
497. "The Interplay Between the Electronic Structure and Reactivity of Aluminum Clusters: Model Systems as Building Blocks for Cluster Assembled Materials," B. D. Leskiw and A. W. Castleman, Jr., *Chem. Phys. Lett.*, **316**, 31-36, (2000).
498. "The Effects of Water Solvation of Double Proton Transfer Reactions," D. E. Folmer, E. S. Wisniewski, and A. W. Castleman, Jr., In *Cluster and Nanostructure Interfaces*, Editors: P. Jena, S. N. Khanna, B. K. Rao, (World Scientific, Singapore, New Jersey, London, Hong Kong 2000), 489-494.
499. "Excited State Double Proton Transfer in the 7-Azaindole Dimer Revisited," D. E. Folmer, E. S. Wisniewski, and A. W. Castleman, Jr., *Chem. Phys. Lett.*, **318**, 637-643, (2000).
500. "Covariance Mapping Studies of 7-Azaindole Fragments," D. A. Card, D. E. Folmer, E. S. Wisniewski, and A. W. Castleman, Jr., In *Cluster and Nanostructure Interfaces* Editors: P. Jena, S. N. Khanna, B. K. Rao, (World Scientific, Singapore, New Jersey, London, Hong Kong 2000), 25-30.
502. "The Interplay Between the Electronic Structure and Reactivity of Aluminum Clusters," B. D. Leskiw and A. W. Castleman, Jr., In *Cluster and Nanostructure Interfaces* Editors: P. Jena, S. N. Khanna, B. K. Rao, (World Scientific, Singapore, New Jersey, London, Hong Kong 2000), 25-30.
504. "Bulk Production, Isolation, and Characterization of Metallocarbohedrenes," M. E. Lyn, G. S. McCarty, D. E. Bergeron, E. R. Statz, A. D. Korman, P. S. Weiss, and A. W. Castleman, Jr., In *Cluster and Nanostructure Interfaces* Editors: P. Jena, S. N. Khanna, B. K. Rao, (World Scientific, Singapore, New Jersey, London, Hong Kong 2000), 25-30.
505. "Ionization Dynamics of Transition Meta - Carbon Clusters," S. E. Kooi, B. D. Leskiw, and A. W. Castleman, Jr., In *Cluster and Nanostructure Interfaces* Editors: P. Jena, S. N. Khanna, B. K. Rao, (World Scientific, Singapore, New Jersey, London, Hong Kong 2000), 25-30.
507. "An Ultrafast Glimpse of Cluster Solvation Effects on Reaction Dynamics," Q. Zhong and A. W. Castleman, Jr., *Chem. Rev.*, **100**, 4039-4057, (2000).
510. "Water Assisted Proton Transfer in the Monomer of 7-Azaindole," D. E. Folmer, E. S. Wisniewski, and A. W. Castleman, Jr., *The Journal of Physical Chemistry A*, **104**, 1054-10549, (2000).
515. "An Ultrafast Look at Cluster Dynamics," A. W. Castleman, Jr., Nobel Symposium on the Physics and Chemistry of Clusters, *World Scientific*, in press.
516. "Femtosecond Lasers and Time of Flight Mass Spectrometry: A Valuable Marriage," L. Poth, Q. Zhong, and A.W. Castleman, Jr., *Proceedings of 15th IMSC: Gas Phase Ion Chemistry: Reaction Mechanisms and Ion Structures*, in press.
517. "Studies of Cluster Dynamics Via Transient Spectroscopy and Coulomb Explosion," L. Poth, Q. Zhong, A. W. Castleman, Jr., *Proceedings of the Atoms, Molecules and Quantum Dots in Laser Fields: Fundamental Processes*, in press.

IIIb. List of Seminars, Posters, Talks, During the Report Period (date of grant) to Present Reporting AFOSR Sponsored Research

- "Clusters: Elucidating the Influence of Solvation on Reaction and Ionization Dynamics," invited lecture, Femtochemistry '97 Conference, Lund, Sweden, August 31-September 4, 1997.
- "Cluster Dynamics: From the Ultraslow to the Ultrafast," invited seminar, Physics/Chemistry Department, Chalmers University, Göteborg University, Sweden, September 5, 1997.
- "Exploring Cluster Dynamics in the Ultrafast Time Regime," 214th ACS National Meeting, Las Vegas, Nevada, September 7-11, 1997.
- "Clusters: Probing the Properties and Dynamics of Intermediate States of Matter," Opening Plenary Address in Celebration of the Millenium of Gdansk, Gdansk, Poland, September 19-22, 1997.
- "Elucidating Dynamical Events in Clusters Using Ultrafast Lasers," invited seminar, The Polish Academy of Science, September 29, 1997.
- "Exploring Cluster Dynamics in the Ultrafast Time Regime," invited speaker, 13th Interdisciplinary Laser Science Conference: Symposium on Laser-Induced Chemistry in Clusters, Long Beach, CA, October 23-17, 1997.
- "Shedding Some Light on Clusters," invited seminar, Department of Chemistry, Indiana University, Bloomington, IN, November 6, 1997.
- "Clusters: Insights into Nucleation and Heterogeneous Chemistry," NASA/Goddard Space Flight Center, Washington, DC, November 20, 1997.
- "An Ultrafast Look at Reactions in Clusters," Gordon Research Conference on Molecular and Ionic Clusters, Ventura, CA, January 4-8, 1998.
- "Clusters: Insights into Nucleation Processes and Heterogeneous Chemistry of Atmospheric Interest," Invited Colloquium, Department of Meteorology, Pennsylvania State University, University Park, PA, January 22, 1998.
- "Production and Analysis of Metallocarbohedrene Containing Soot," (poster presented by Brian J. Toleno), 215th National Meeting of the American Chemical Society, Dallas, TX, March 23-April 2, 1998.
- "Shedding Some Light on Met-Cars: A Unique Class of Molecular Clusters," invited colloquium, Department of Chemistry, Louisiana State University, Baton Rouge, LA, March 20, 1998.
- "Shedding Some Light on Met-Cars: Prospective Building Blocks of New Materials," invited seminar, Physics Department, Virginia Commonwealth University, Richmond, VA, April 2, 1998.
- "Shedding Some Light on Met-Cars: A Unique Class of Molecular Clusters," invited colloquium, Department of Chemistry, Johns Hopkins University, Baltimore, MD, April 16, 1998.

- "Atmospheric Studies Using Cluster Ions," (talk presented by John Gilligan), The First Environmental Symposium, Pennsylvania State University, University Park, PA, April 18, 1998.
- "Clusters: Prospects of Building Blocks for New Materials," invited colloquium, Department of Chemistry, University of Rochester, Rochester, NY, April 29, 1998.
- "Clusters: Prospects of Building Blocks for New Materials," invited seminar, Argonne National Laboratory, Argonne, IL, May 4, 1998.
- "Shedding a Little Light on Clusters," invited seminar, Ohio State University, Columbus, OH, May 11, 1998.
- "Femtosecond Studies of Solvation Effects on Competitive Reactions in Clusters," invited talk, 23rd Informal Conference on Photochemistry, Pasadena, CA, May 10-14, 1998.
- "Optical Excitation, Ionization and Reactive Dynamics of Molecular Clusters," invited talk, Air Force Molecular Dynamics Contractor's Meeting, Monterey, CA, May 17-20, 1998.
- "Solvation Effects on Reactions in Clusters," invited talk, International Conference on Water in the Gas Phase, Paris, France, June 21-24, 1998.
- "An Ultrafast Look at Reaction Dynamics in Clusters," invited seminar, Physics Department, University of Innsbruck, Austria, July 6, 1998.
- "Exploring the Coulomb Explosion Phenomena with Covariance Mapping," (poster presented by Dennis A. Card), Ninth International Symposium on Small Particles and Inorganic Clusters, Lausanne, Switzerland, September 1-5, 1998.
- "Clusters: Prospects for New Materials," invited seminar, Physics Department, University of Wuerzburg, Germany, October 21, 1998.
- "Atomic and Molecular Clusters: Prospects for New Materials," invited colloquium, Association of German Chemists, Technische Universitaet Darmstadt, Germany, October 27, 1998.
- "Met-Cars: A Unique Class of Molecular Clusters," invited colloquium, Gesellschaft Deutscher Chemiker, E.V. Johann Wolfgang Goethe-Universitaet, Frankfurt am Main, Germany, October 28, 1998.
- "Latest Findings on the Photoionization of Met-Cars" (talk presented by H. Sakurai), Seventh Consortium on Nanostructure Materials, Richmond, Virginia, October 30, 1998.
- "Overview of Cluster Research at Penn State," Max Planck Institut fuer Festkoerperforschung, Stuttgart, Germany, November 3, 1998
- "Arresting Intermediate States via Coulomb Explosion in the 7-Azaindole Dimer" (talk presented by D. E. Folmer), Max Planck Institut fuer Festkoerperforschung, Stuttgart, Germany, November 3, 1998.
- "Thermionic Emission in Transition Metal Carbon Clusters: Experimental and Theoretical Investigations" (talk presented by S. E. Kooi), Max Planck Institut fuer Festkoerperforschung, Stuttgart, Germany, November 4, 1998.

- "Reaction and Ionization Dynamics of Clusters in the Ultrafast Time Regime," Max Planck Institut fuer Stroemungsforschung, Goettingen, Germany, November 6, 1998.
- "Ionization Dynamics of Clusters in the Ultrafast Time Regime," Max Born Institut fuer Nichtlinear Oiptik und Kurzzeitspektroskopie, Berlin, Germany, November 9, 1998.
- "Met-Cars: A Unique Class of Molecular Clusters," Fritz Haber Institut der Max Planck Gesellschaft, Berlin, Germany, November 10, 1998.
- "Reaction and Ionization Dynamics of Clusters in the Ultrafast Time Regime," Physics Department, Freie Universitaet Berlin, Berlin, Germany, November 11, 1998.
- "The Ionization Dynamics of Met-Cars," International Workshop on the Structure and Dynamics of Metallic Clusters, Berlin, Germany, November 12-14, 1998.
- "Cluster Dynamics: From the Ultraslow to the Ultrafast," invited seminar, Physics Department, University of Wuerzburg, Germany, November 25, 1998.
- "Studies of Cage-Like Aggregates: From Outer Space to the Condensed State," invited colloquium, Physics Department, University of Konstanz, Germany, December 1, 1998.
- "Dynamics of Reactions in Clusters," invited colloquium, Institute fuer Festkoerperforschung, Forschungszentrum Juelich, Germany, December 7, 1998.
- "Met-Cars: A Unique Class of Molecular Clusters and Prospects for New Materials," invited colloquium, Institute fuer Festkoerperforschung, Forschungszentrum Juelich, Germany, December 7, 1998.
- "Reaction and Ionization Dynamics of Clusters in the Ultrafast Regime," Chemistry Department Seminar, University of Florida, Gainesville, January 12, 1999.
- "Met-Cars: A Unique Class of Molecular Clusters", Quantum Theory Project Seminar, University of Florida, Gainesville, January 13, 1999.
- "Met-Cars: A Unique Class of Molecular Clusters," National High Magnetic Field Laboratory (NHMFL) Seminar, Florida Sate University, Tallahassee, January 14, 1999.
- "Reaction and Ionization of Clusters in the Ultrafast Time Range," Chemistry Department Seminar, Florida State University, Tallahassee, January 15, 1999.
- "Met-Cars: A Unique Class of Molecular Clusters," Department of Chemistry Seminar, Iowa State University, Ames, IA, February 18, 1999.
- "A Fast Explosive Look at Ion Molecule Reactions in Clusters," invited speaker, The 1999 Robert Squires Gordon Research Conference on Structure, Energetics, and Dynamics of Gaseous Ions, Ventura, CA, February 28 - March 4, 1999.
- "Probing Cluster Dynamics in the Ultrafast Time Domain," invited speaker, The Cluster Spectroscopy and Dynamics Symposium at the Centennial American Physical Society meeting, Atlanta, GA, March 21-26, 1999.
- "Reaction and Ionization Dynamics of Clusters in the Ultrafast Time Regime," invited Seminar, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, May 5, 1999.

- "Atomic and Molecular Clusters: Matter of Nanoscale Dimensions," Physics Division Colloquium, Argonne National Laboratory, Artonne, IL, May 14, 1999.
- "The Influence of Solvation on the Dynamics of Cluster Reactions," invited talk, International Symposium on Molecular Clusters, Munich, Germany, May 25-29, 1999.
- "Clusters: Properties and Prospects for New Materials," Physics Department Colloquium, University of Innsbruck, Austria, June 16, 1999.
- Lecture Series on Clusters: Institut fuer Ionen Physik, University of Innsbruck, Austria.
(a) "Why Study Clusters: What do They Teach Us?", June 17, 1999; (b) "Matter of Nanoscale Dimensions", June 18, 1999; (c) "Probing Cluster Dynamics with Ultrafast Lasers", June 24, 1999; (d) "Some Contemporary Problems in Atmospheric Science. June 25, 1999.
- "Dynamics of Ionization Processes in Clusters," Department of Physics Seminar, University of Innsbruck, Austria, June 23, 1999.
- "Investigating Reaction Dynamics in Clusters via Coulomb Explosion," invited talk, Femtochemistry-IV 1999, Leuven, Belgium, July 18-22, 1999.
- "Probing Cluster Dynamics via Coulomb Explosion," invited talk, 1999 OSA Annual Meeting & Exhibit: Optics in High-Tech Industries," Santa Clara, CA, September 26-30, 1999.
- "In Memory of My Former Postdoctoral Research Associate, Colleague, and Friend, Derek Lindsay," invited talk, 1999 Memorial Service, New York, NY, October 21, 1999.
- "Cluster Dynamics: Coulomb Explosion and Reaction Phenomena," invited lecture, International Symposium on Clusters and Nanostructures, Richmond, VA, October 25-28, 1999.
- "The Effect of Hydration on the double Proton Transfer Reaction in 7-Azaindole Dimers," (poster presented by D. E. Folmer), International Symposium on Clusters and Nanostructures, Richmond, VA, October 25-28, 1999.
- "Photochemistry of Transition Metal Containing Clusters," (poster presented by S. E. Kooi), International Symposium on Clusters and Nanostructures, Richmond, VA, October 25-28, 1999.
- "Stability, Ionization Potentials, and Geometry of Metallocarbohedrenes," (poster presented by H. Sakurai), International Symposium on Clusters and Nanostructures, Richmond, VA, October 25-28, 1999.
- "Bulk Production, Isolation, and Characterization of Metallocarbohedrenes," (poster presented by M. E. Lyn) International Symposium on Clusters and Nanostructures, Richmond, VA, October 25-28, 1999.
- "An Ultrafast Look at Reactions in Clusters: Resolving Issues in Atmospheric Chemistry, Materials and Catalytic Science, and Radiation Biology," invited talk, EMSL Molecular Theory Workshop, Richland, WA, November 7-10, 1999.
- "Solvation effects on the excited state double proton transfer in 7-azaindole," (poster presented by D. E. Folmer) ACS Meeting, San Francisco, CA, March 29, 2000.

- "Ultrafast Dynamics in Molecular Clusters," (talk presented by S. Kooi) PASI 2000 meeting, Angra dos Reis, Brazil, April 25 – May 8, 2000.
- "An Ultrafast Glimpse of Coulomb Explosion and Solvation Effects on Reaction Dynamics in Clusters," Chemistry Department Colloquium at Brown University in Rhode Island, May 12, 2000.
- "Cluster Dynamics: Following Reaction Intermediately Using Coulomb Explosion Ion Imaging Phenomena," 33rd ACS Middle Atlantic Regional Meeting, Newark, DE, May 15, 2000.
- "Fragmentation and Ionization Dynamics of Molecular Clusters: Applications of Mass Spectrometry," (talk presented by S. Kooi), 33rd ACS Middle Atlantic Regional Meeting, Newark, DE, May 15, 2000.
- "An Ultrafast Look at Cluster Dynamics," A. W. Castleman, Jr., Plenary Lecture at the Nobel Symposium on the Physics and Chemistry of Clusters, Visby, Sweden, June 27 – July 2, 2000.
- "Ultrafast Look At Cluster Dynamics," (invited talk), SFB Colloquium Freie University of Berlin, July 11, 2000.
- "Laying the Foundations for Developing Cluster Assembled Nanoscale Materials," (invited talk), Chemical Physics Seminar, Freie University of Berlin, July 12, 2000.
- "Dynamics of Transition Metal Oxides," (invited talk), SFB Colloquium, Humboldt-University at Berlin, July 14, 2000.
- "The Formation and Ionization Dynamics of Met-Cars, (invited talk) Organic/Inorganic Chemistry Seminar, Technische University of Berlin, July 18, 2000.
- "Cluster Reactions: An Approach to Elucidating the Physical Basis of Heterogeneous Catalysis," (invited talk), 11th DOE/BES Heterogeneous Catalysis and Surface Science Meeting, Rockville, MD, August 16-18, 2000.
- "The Influence of Hydration on the Dynamics of Proton Transfer Reactions," (invited talk), 220th National ACS Meeting (Nobel Symposium In honor of Zewail), Washington, DC, August 20-24, 2000.
- "Femtosecond Lasers and Time-of-Flight Mass Spectrometry: A Valuable Marriage," (invited talk), Keynote Lecture at the 15th IMSC, Barcelona, Spain, August 27 – September 1, 2000.

Consultative and advisory functions:

DuPont Consultantship
Subject Area: Formation and Properties of Small Oxide and Carbide
Cluster Materials

Transitions:

Several industries have expressed interest in Met-Cars, which were discovered in our laboratory and have been found to display unusual ionization and reactive properties. These include:

1. *General Sciences, Incorporated* (205 Schoolhouse Road, Souderton, PA 18964)

We are exploring with them potential uses of the material and ways of scaling up its production.

2. *DuPont Company*

DuPont has expressed some interest in Met-Cars as potential catalysts, though their main interaction with us deals with small oxide clusters where there is a more immediate application to their current catalytic needs. This interaction has resulted in the commencement or collaborative work on catalysis and the pursuit of a joint grant between DuPont and ourselves through the GOALI-NSF program, approved and funded May 1, 1996.

DuPont has expressed interest in Met-Cars, which were discovered in our laboratory, and other metal compound clusters that have been found to display unique ionization and reactive properties. The company has expressed particular interest in Met-Cars as potential catalysts, though their main interaction with us deals with small oxide clusters where there is a more immediate application to their current catalytic needs. This interaction has resulted in the commencement of collaborative work on catalysis and the pursuit of a joint grant between DuPont and ourselves through the GOALI-NSF program.

Intel Corporation has expressed interest in our nanoscale materials work and has agreed to donate equipment valued at about \$ 4 million dollars to help facilitate our activities in this area. DuPont has expressed interest in Met-Cars, which were discovered in our laboratory, and other metal compound clusters that have been found to display unique ionization and reactive properties. The company has expressed particular interest in Met-Cars as potential catalysts, though their main interaction with us deals with small oxide clusters where there is a more immediate application to their current catalytic needs. This interaction has resulted in the collaborative work on catalysis and the pursuit of a joint grant between DuPont and ourselves through the GOALI-NSF program.

3. *Intel*

\$4.5 Million worth of equipment donated to my laboratory to be used in preparing supported clusters.

New Discoveries, Inventions, or Patent Disclosures:

Developed a new method of "freezing" and studying intermediates in a chemical reaction: see publications 465 and 494 listed above.

The method we developed to "freeze and study intermediates in fast reactions was chosen to be featured in the Encyclopedia Britannica: Yearbook of Science and the Future 2000, pgs 246-247, Encyclopedia

Britannica, Inc. Chicago, and on the cover of the Proceedings of the National Academy of Sciences, November 9, 1999, vol. 96.

Honors:

Elected Member, National Academy of Sciences in 1998
Elected Fellow, American Academy of Arts and Sciences in 1998
Elected Fellow, New York Academy of Sciences in 1998
Named Editor-in-Chief of new book series dealing with *Clusters* (with emphasis on Materials Science), Springer-Verlag Publisher in 1998
Appointed the Eberly Distinguished Chair in Science, The Pennsylvania State University in 1999
Doktors Honoris Causa, University of Innsbruck, Austria
Named Evan Pugh Professor of Chemistry, the highest honor that The Pennsylvania State University bestows on a faculty member
Senior Editor, *Journal of Physical Chemistry*
Fellow of the American Association for the Advancement of Science
Fellow of the American Physical Society
Honorary Society Member of Sigma Xi, Phi Lambda Upsilon